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An integrated approach to evaluate the leaching behaviour of silver from sulfide concentrates

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Abstract

The leaching rates of two different mineral concentrates with the same silver content were investigated by cyanide leaching with silver phases identified by scanning electron microscopy (SEM) and electrochemical analysis. The mineralogical characterization (SEM) of the concentrates showed that each contained the silver in different phases. After leaching, the disappearance of only one of the phases in each concentrate was detected. The remaining silver was contained in phases that are refractory to cyanidation. Simultaneously, an electrochemical method for the detection of the different leachable and refractory silver phases in concentrates and leach residues was developed. Cyclic voltammetry was employed with the concentrate-carbon paste electrodes (concentrate-CPE) in order to detect the oxidation of the different phases of silver contained in the mineral concentrates. The extreme sensitivity of this method allowed the rapid and reliable detection of small quantities of silver, as well as the evaluation of its refractory nature.

1. Introduction

For over 100 years the extraction of precious metals, such as gold and silver, has been carried out by cyanidation [1–3]. However, there still exist many questions regarding the mechanisms involved and the optimum conditions for the process. Kinetic investigations of silver extraction have addressed this problem using two different approaches: chemical and electrochemical. The chemical studies have quantified some aspects, including the pH dependence of the complexes formed [2, 4, 5] and the stoichiometric relations of the leaching reaction [6]. On the other hand, in the electrochemical studies, optimum cyanide–oxygen ratios have been determined using rotating discs [1, 7] and the influence of other metals contained in the leaching solution on passivation or acceleration of the gold and silver extraction has been investigated [8–11]. However, little has been done to integrate both types of research and to identify the chemical phenomena that occur during the leaching of different mineral concentrates. According to the origin of each concentrate, it may contain the silver in different mineral phases, which impact on the quantity and velocity of its extraction.

In electrochemical studies, it is common to detect the total redox processes, as well as the characteristic kinetic parameters, of pure metals. Despite this, the behaviour of the different silver phases contained in mineral concentrates has not been determined since silver is present as sulfides in minute quantities. Also, the difficulty to identify the processes in which silver is involved is due to the fact that other metallic sulfides are contained in the concentrates and these mask the results.

In the present study, proven electrochemical methods are employed to gain knowledge about the oxidation and reduction processes of silver that take place during concentrate cyanidation. As was mentioned above, much of the previous electrochemical research was developed using metallic silver working electrodes [9, 12], which do not reflect the true behaviour of the silver contained in a mineral sulfide concentrate.

To obtain reliable, reproducible results pertaining to the silver phases present in the concentrates, carbon paste electrodes with the electroactive species were used. These electrodes have been widely employed by other authors [13–16] and been shown to represent the actual situation in the system. Cyclic voltammetry was used in the present study because it allows identification of the redox processes that occur in cyanidation.

The mineralogical and electrochemical characterization was performed before and after leaching for two different concentrates, which contain 1.2% of total silver. The objective was to identify the distinct silver phases and to determine which may be refractory, employing a rapid technique that does not require lengthy reaction times.

2. Experimental methods

2.1. *Mineralogical characterization*

The method used to determine the quantity of each metal contained in the concentrate consisted in digesting a known quantity of mineral in aqua regia for the determination of Au, Zn and Fe, and in nitric acid for Ag, Cu and Pb. The analysis of dissolved metals was carried out using a Varian SpectrAA-20 atomic absorption spectrometer (AAS).

For SEM (scanning electron microscope) analysis, the concentrate and residue samples were assembled in a resin. They were then polished and covered with carbon. The samples were observed in a Phillips XL30 SEM. The silver species identification was performed by microanalyses, using energy dispersive X-ray spectrometer (EDAX DX-4) coupled to the SEM. The microanalyses were automatically corrected by the ZAF method.

2.2. *Cyanidation conditions*

Leaching experiments were performed on sulfide concentrates provided by two companies: Real del Monte y Pachuca, S.A. de C.V. [6], and Minera Las Torres, S.A. de C.V., located in Hidalgo and Guanajuato, México, respectively. For this study, the $-200+300$ mesh fraction (52–74 μm) of both concentrates was employed. Pure oxygen was used as an oxidizing agent. Before preparing the cyanide solutions, water was first deionized, boiled for 20 min and cooled to 20 °C. Nitrogen was then sparged for 50 min to ensure that the dissolved CO_2 was liberated. Once the water was free of CO_2, it was used to prepare the cyanide solution and finally the pH was adjusted to 10.6 with NaOH.

The cyanide solution was placed in a standard 1 litre Pyrex reactor, fitted with four ports: one for sampling, another for the introduction of the oxidizing agent, the third for the gas purge and the last for the mixer. The flow of the oxidizing agent was then initiated. After 30 min, the reaction was started by introducing the concentrate. Samples of the solution were extracted at pre-established time intervals and analysed for silver by AAS.

The kinetic experiments lasted for 8 h. The amount of concentrate used was 10 g l^{-1} of solution and the cyanide concentrations were 0.1 and 0.3 M. The temperature was 20 °C. At the end of each experiment, the residues were filtered, dried and analysed for silver to complete the metallurgical balance.

2.3. *Electrochemical analyses*

In the electrochemical studies, two more concentrates were employed in addition to those from Real del Monte and Las Torres for the purpose of comparison. Fresnillo is a relatively pure pyrite concentrate and Echo Bay (Canada) is an Acanthite concentrate.

The cyanide solution was prepared in the same manner as in the leaching studies. The concentration used was 0.3 M NaCN with the pH adjusted to 10.60. An electrochemical cell was fitted with three ports: one for the reference electrode (mercury oxide, $Hg/HgO_{(s)}/$ 1 M KOH, represented in this work as HgO, $E = 0.925$V vs SHE according to [17]) in a Luggin capillary, another for the working electrode (carbon paste-electroactive species) and the last for the counter electrode (graphite bar, Alfa Aesar, Johnson Matthey 99.9995%). The cell was immersed in a constant temperature bath at 20 °C and the system was connected to an EG&G PAR 273 machine.

The working electrode was prepared according to [16] by mixing 0.7 g natural graphite powder (Alfa Aesar, 2–15 μm, 99.9995%), 0.3 g of the electroactive species (concentrates from Las Torres, Real del Monte, Fresnillo and their respective leached residues and Acanthite from Echo Bay Mine) and silicone oil in an agate mortar to a homogeneous paste. The silicone oil (Sigma, $\rho = 0.96$ g ml,$^{-1}$ $v = 200$ cS) quantity depended on the concentrate in use. Once the paste was ready, it was introduced into a 7 cm long, 0.2 cm interior polyethylene syringe. A platinum with copper (silver welded) wire was used as the electrical contact. Immersion tests were applied to the concentrate-CPE in the electrolyte to determine the time independence of the OCP (open circuit potential), which is referred by some authors as the surface preconditioned time [13]. The OCP values for the concentrates and their leached residues, respectively, are: Real del Monte -125 and -20 mV; Las Torres -165 and -145 mV; Pyrite -145 and -135 mV; and Acanthite -355 mV (unleached only).

The cyanide solution (electrolyte) was added to the electrochemical system and nitrogen was bubbled for 20 min. After this time the flow direction was switched over the electrolyte, in order to keep an inert atmosphere during the experiment. The working electrode was then introduced into the cell, insuring that the paste was in contact with the electrolyte. After each voltammetric scan, the electrode was washed with deionized water and the surface renewed, in order to eliminate the carbon paste that had been in contact with the electrolytic solution. The carbon paste was compacted and polished using a Carbimet Piper disc (Buhler 600).

3. Results and discussion

3.1. *Chemistry and mineralogy of the concentrates*

The chemical analysis results for the four concentrates used are shown in Table 1. The amount of silver contained in the first two concentrates is very similar, although the iron content present in Las Torres is higher than that in Real del Monte.

The SEM studies showed a great difference between the silver phase found in both concentrates. For the concentrate from Real del Monte, only silver sulfide was

Table 1. Metal percent (%) present in each concentrate and mineral

Metal	Las Torres	Real del Monte (Luna and Lapidus, 2000)	Fresnillo	Echo Bay
Silver	1.23	1.20	n.a	86.27
Copper	0.93	0.27	0.62	0.87
Lead	0.47	0.92	n.a	0.0
Iron	37.95	21.40	47.80	2.54
Zinc	0.66	0.47	n.a	0.0
Gold	80.80*	7.25*	n.a	0.0

*g Au/ton mineral; n.a not analysed.

Table 2. Silver phases contained in the Las Torres concentrate

Silver species	Formula	Relative abundance
Aguilarite	Ag_4SeS	80.4%
Freibergite	$(Cu, Ag, Zn, Fe)_{12}.Sb_4\ S_{13}$	14.3%
Polybasite	$9Ag_2S.Sb_2S_3$	3.9%
Hessite	Ag_2Te	1.4%
	Total	100.0%

observed (acanthite, [18, 19]) as may be seen in Figure 1(a) before cyanidation. In this Figure, the silver sulfide may be clearly differentiated as a brilliant phase, liberated from other metals.

After leaching the concentrate with 0.3 M cyanide, the residue was analysed in order to observe the phases that remained (3% of the original silver). Figure 1(b), shows the SEM results where it may be observed that the small amount of silver sulfide present in the residue was occluded in other mineralogical phases, such as galena or pyrite. This means that 97% of the acanthite is leached.

In the case of the Las Torres concentrate, the silver phases are shown in Table 2. Four separate phases were found, the most abundant of which was aguilarite (80%). In Figure 2(a), this phase is shown, liberated and of a large size, before the leaching takes place. The grain size (60 μm) is similar to that found for the acanthite in Real del Monte (50 μm), the difference being that the aguilarite contains selenium in addition to sulfur.

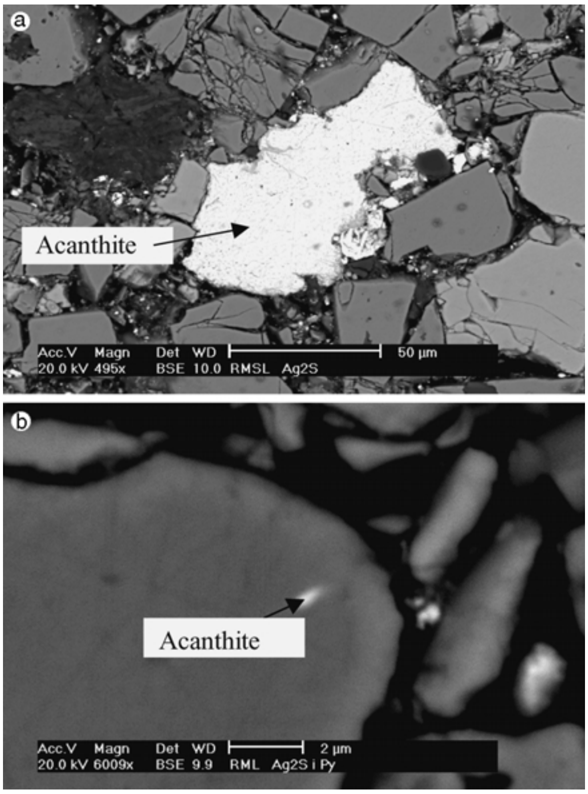

Fig. 1. Scanning electron microscopy image of Real del Monte concentrate. Acanthite is shown (a) before and (b) after leaching.

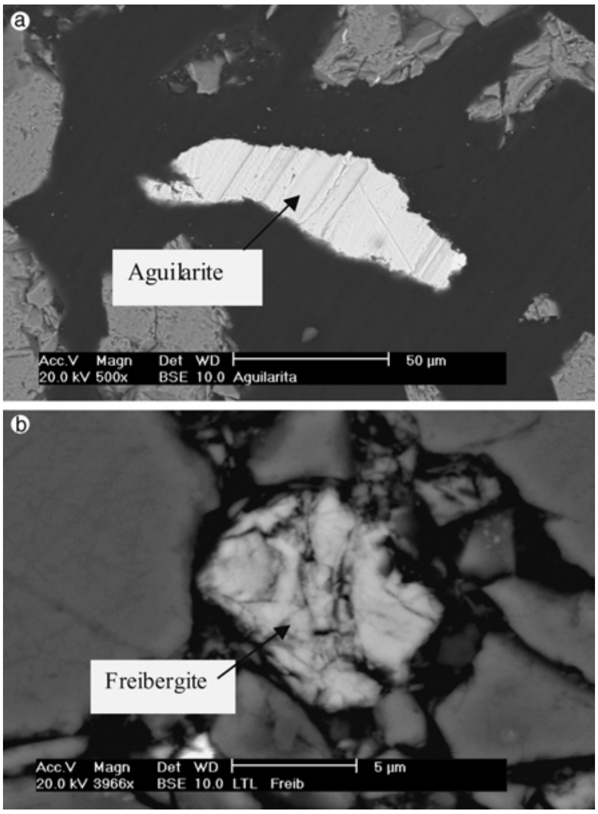

Fig. 2. Scanning electron microscopy image of Las Torres concentrate. (a) Before (aguilarite) and (b) after leaching (residue) freibergite.

Analysis of the Las Torres residue, after leaching with 0.3 M cyanide, revealed that the only phase extracted was free aguilarite and not the others. This may be observed in Figure 2(b), where freibergite, the second in abundance after aguilarite, is shown. The luster of freibergite is less than that of aguilarite, and there is a difference in morphology (rounded for the freibergite and elongated for the aguilarite). The effect of this phase on the final silver extraction percentage is large since it constitutes 14% of the silver in the concentrate. Its refractory nature is a consequence of the large particle size, as well as its chemical composition.

3.2. *Leaching behaviour of silver sulfide contained in two different sulfide concentrates*

In the SEM characterization, the leachable phases were determined. Therefore, in the case of the Las Torres concentrate, aguilarite was found to represent 100% of the leachable phases. On this basis, all conversions in the following two figures for both concentrates were normalized to account for only the leachable phases: free acanthite (97%) for Real del Monte and aguilarite (80%) in Las Torres.

The extractions obtained for each concentrate are presented in Figure 3 as silver conversion versus time at two different cyanide concentrations. The sample from Real del Monte shows a rapid silver conversion at both concentrations, while the concentrate from Las Torres is much slower. The extraction tendencies for both concentrates in 0.1 M cyanide are similar (Figure 3(b)), however, after 8 h of reaction there is a divergence of 17%, even with normalization. In 0.3 M cyanide (Figure 3(a)), the trends are completely different for each concentrate because Real del Monte reaches the maximum conversion within a few minutes while the Las Torres follows a pattern similar to the other cyanide concentration. From this, it may be implied that oxygen oxidized the selenide ions (aguilarite) at a different rate than it does with the sulfide ions (acanthite).

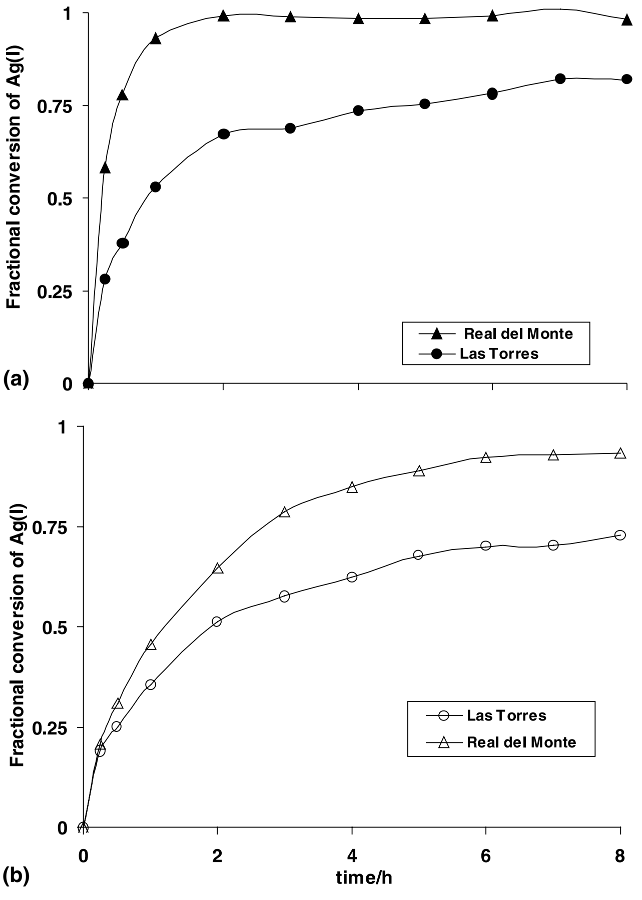

Fig. 3. Comparison between the leaching behaviour of two different concentrates at two (10 g of concentrate L^{-1} leach solution) cyanide concentrations and $T = 20$ °C. (a) 0.3 M NaCN and (b) 0.1 M NaCN. Normalized to 100% of the leachable phase; acanthite in Real del Monte and aguilarite in Las Torres.

3.3. *Voltammetric studies*

One of the objectives of this study is to present a methodology to distinguish oxidizable (leachable) silver phases in a rapid, qualitative and reliable manner, employing electrochemical systems. Cyclic voltammetry is a tool that permits identification of oxidative and reductive processes that take place at the solid–liquid interface of a microscopic system and was used in this work to detect the silver minerals in different concentrates. The establishment of the redox reactions that occur during cyanidation in electrochemical systems is of great importance; however, due to the complexity of the present study because of the presence of different chemical species and mineral phases, such as lead, copper and zinc contained in the concentrates, these are still under investigation and will form part of a future study.

Carbon paste electrodes (CPE) were exclusively employed in this work. The reproducibility of the results in the voltammetric studies using concentrate-CPE has been confirmed by various authors [14–16]. The advantages of this technique may be attributed to the homogeneity of the paste (natural graphite powder and concentrate) and the surface renewal after each voltammetric sweep. This method avoids the problems of reproducibility that arise when mineral crystals are used as the working electrode.

Since the two concentrates under study (Real del Monte and Las Torres) contain the silver in distinct mineral phases and the pyrite in different amounts, the voltammetric research was first performed on high purity concentrates of silver sulfide and pyrite (the Echo Bay concentrate consists of 98% Acanthite and the Fresnillo concentrate is 97% pyrite). This was done with the intention of establishing the behaviour of two limiting cases: silver sulfide and pyrite.

For the determination of the processes that occur in the acanthite, pyrite, Real del Monte and Las Torres concentrates, the potential sweep was initiated in the positive direction starting from the OCP up until 1200 mV vs HgO. At this value, the potential sweep was reversed to the cathodic direction, until it reached −1200 mV, where it was again reversed. The sweep was ended at the value of the OCP. It is important to emphasize that in all the work presented here, the potentials are referred to the HgO (mercury oxide, Hg/$HgO_{(s)}$/1 M KOH, $E = 0.925$ V vs SHE) electrode. This was selected to avoid contamination from chloride ions, as well as to prevent the formation of undesirable sulfur species.

In Figure 4, typical voltammetric responses of the acanthite and pyrite concentrates are shown. The first oxidation process in the pyrite (Figure 4(b)) starts at potentials of less than 600 mV vs HgO, while the acanthite (Figure 4(a)) only begins to exhibit oxidation at 900 mV vs HgO. When $E = 600$ mV, the current associated to direct oxidation of pyrite is 37.6 μA, meanwhile in acanthite the current value at same

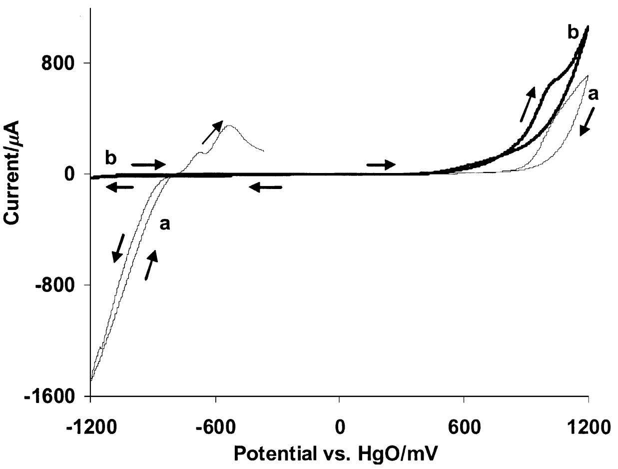

Fig. 4. Typical cyclic voltammograms obtained for the concentrate-CPE (30 wt %) in aqueous solution, $[CN^-]=0.3$ M, pH 10.60. Concentrates employed: (a) acanthite, (b) pyrite. Sweep potential direction initiated from the OCP towards the positive direction and $v = 25$ mV s^{-1}.

potential is 10.1 μA. On inversion of the potential sweep, the pyrite continues to be oxidized, while for the acanthite the current behaves differently from that that of pyrite. This behavior indicates that the nature of the oxidation products is electrically different. It is important to note in the anodic part of the sweep, that the oxidation process of the pyrite most likely masks that of the silver sulfide when the two are present in the same concentrate, especially in those concentrates which contain only small amounts of silver sulfide or other silver phases. When the potential sweep reaches the cathodic zone, the pyrite exhibits no significant reductive process. Meanwhile, the acanthite displays a very important reductive response related to the reduction of the silver ions, produced in the oxidation process. When the sweep was inverted again, two more peaks were detected, which may be attributed to the reoxidation of metallic silver. The large differences which exist between the behaviour of acanthite and pyrite in the reduction zone, should permit the identification of the oxidizable and reducible species in the Real del Monte and the Las Torres concentrates.

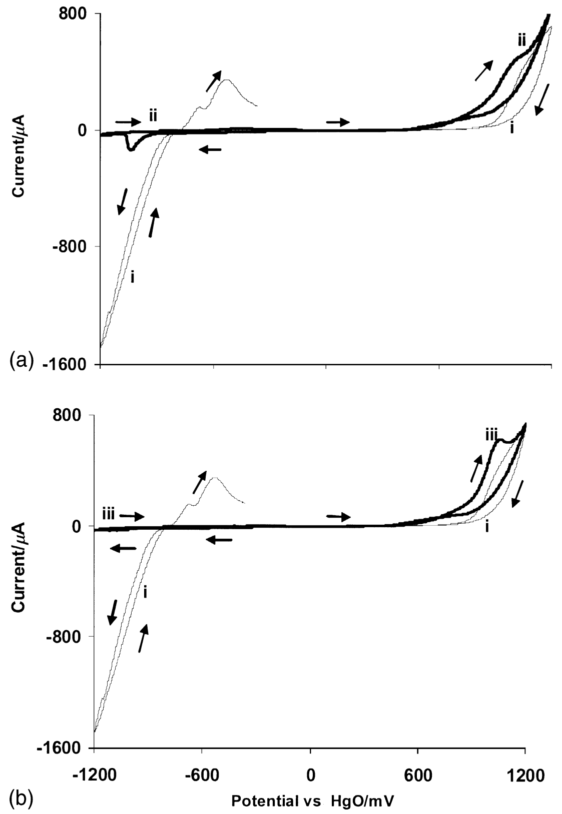

Fig. 5. Typical cyclic voltammograms obtained for the concentrate-CPE (30 wt %) in aqueous solution, $[CN^-]=0.3$ M, pH 10.60. (a **ii**) Real del Monte, (b **iii**) Las Torres. Fine line shows the voltammetric behaviour of the acanthite (**i** in a and b). Sweep potential direction initiated from the OCP towards the positive direction and $v = 25$ mV s^{-1}.

Figure 5 shows typical voltammetric responses for the Real del Monte (Figure 5(a) **ii**) and the Las Torres (Figure 5(b) **iii**) concentrates with respect to acanthite (Figure 5(a)**i** and (b)). In Figure 6 the same comparisons were made with pyrite. In the direct potential sweep for both concentrates (**ii** and **iii**) the oxidation processes begin at potentials less than 600 mV vs HgO. This is similar to where pyrite begins oxidation (Figure 6(a)**i**) and is much less positive than where acanthite (Figure 5(a) **i** and (b) **i**) begins oxidation. In the Real del Monte and Las Torres concentrates, the response due to the oxidation of silver sulfide is not easily distinguishable because it is completely overshadowed by the processes occurring in pyrite. In the inverse sweep in the cathodic zone, for Real del Monte, a small peak starting at −900 mV is observed (Figure 5(a) **ii**), while that peak is much more difficult to detect in Las Torres (Figure 5(b) **iii**). For both concentrates, the oxidation processes are similar to those of pyrite (Figure 6), although the lower intensity is due to the smaller quantities of iron sulfide. In Figure 7 the cathodic zone of the voltammograms of Figure 6 have been amplified. When the inverse potential sweep is applied, the formation of only one small peak (peak I in Figure 7 **i**) may be noted for pyrite. This peak is also observed in the concentrates (Figure 7 **ii**) and is assumed to be related to the reduction of the iron species that were produced during the direct sweep. However, a second peak (peak II, Figure 7 **ii** and **iii**) is formed at more negative potentials for only the concentrates and which corresponds to reduction of silver ions liberated in the direct sweep. In Real del Monte (Figure 7 **ii**), peak II initiates at −900 mV, in a lesser quantity, but similar in behavior to the acanthite (Figure 5(a) **i**). When the sweep potential is inverted, there is a reoxidation of the metallic silver formed. With respect to Las Torres (Figure 7 **iii**), the quantity of silver ions is even less than that reduced in Real del Monte (Figure 7 **ii**), which may mean that less of the silver contained in this concentrate has been electrochemically oxidized.

It is very important to mention that even though both concentrates contained only 1.2% silver, it is possible to

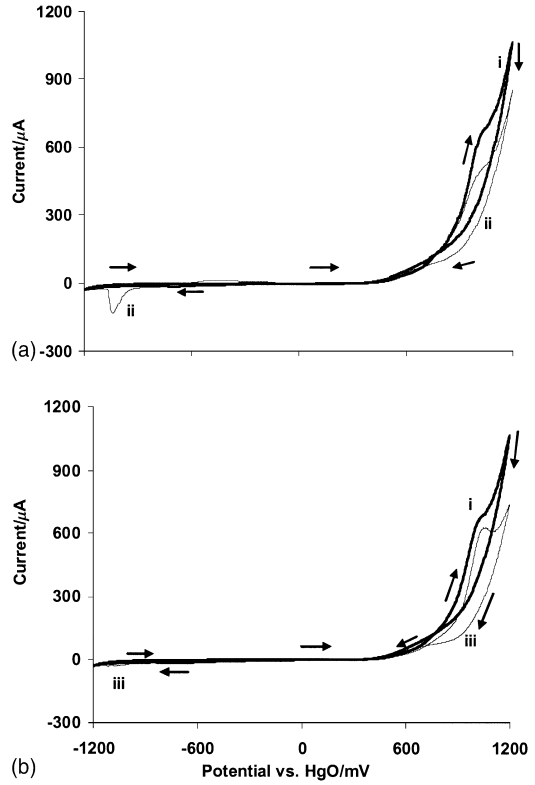

Fig. 6. Typical cyclic voltammograms obtained for the concentrate-CPE (30 wt %) in aqueous solution, $[CN^-]=0.3$ M, pH 10.60. Concentrates without leaching: Pyrite (**i** in a and b), Real del Monte (**ii** in a) and Las Torres (**iii** in b). Sweep potential direction initiated from the OCP towards the positive direction and v = 25 mV s^{-1}.

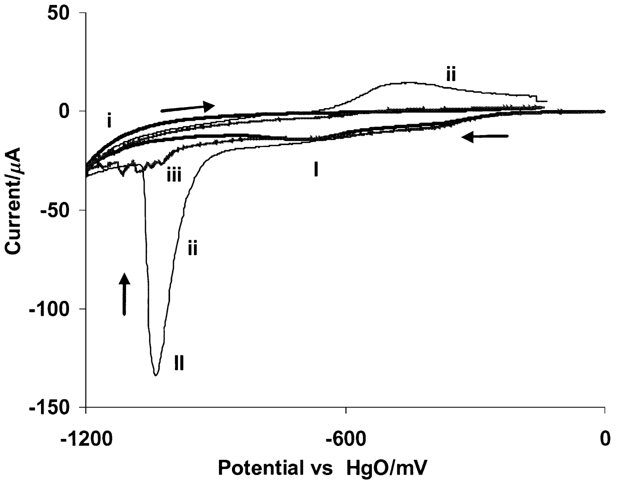

Fig. 7. Typical cyclic voltammograms obtained for the concentrate-CPE (30 wt %) in aqueous solution, $[CN^-]=0.3$ M, pH 10.60. Concentrates without leaching: (**i**) Pyrite, (**ii**) Real del Monte and (**iii**) Las Torres. The sweep potential direction was initiated from the OCP towards the positive direction and v = 25 mV s^{-1}. Cathodic zone in the voltammograms of Figure 6 has been amplified.

detect, by the voltammetric studies, the presence of the different silver phases (Section 3.2) contained in the concentrates. The similar behaviour between Real del Monte and the acanthite can be attributed to the fact that, in the former, only silver sulfide was observed (Section 3.1), while in Las Torres, four silver phases were noted, the most abundant being aguilarite.

The same voltammetric studies shown above were applied to the leached residues to electrochemically detect the disappearance of the most easily oxidizable silver phases (acanthite in Real del Monte and Aguilarite in Las Torres). Figure 8 shows only the cathodic zones of the voltammograms obtained for the pyrite, Real del Monte and Las Torres leached residues (Section 2.2). In the anodic zone (not shown in Figure 8), the oxidation processes are again similar to those that appear in Figure 6, although of less intensity because the concentrates have been leached. On inversion of the potential sweep in the cathodic zone (Figure 8), the reduction peak (II), which was associated with the reduction of silver ions in Figure 7(c), has vanished. In its place, the voltammetric responses of Real del Monte and Las Torres residues are notably similar to the behaviour shown by the reduction processes of the pyrite residue (Figure 8(a)). This indicates that all of the silver contained in the Real del Monte concentrate was extracted during the leaching process (Section 3.2). However, the remaining silver still present in Las Torres is not easily detected by this technique.

During the comparative study applied to the voltammetric responses of the concentrates and their residues, it was difficult to differentiate the oxidation processes of the different silver species in the anodic zone: this was attributed to the masking effect of the iron sulfide. Nevertheless, it was possible to identify the presence of the silver contained in the concentrates by voltammogram analysis in the cathodic zone. To establish a methodology for this identification, a similar voltammetric study was carried out on the concentrates and their residues. However, in this case, the positive sweep started from the OCP until a specific value of E_λ, where

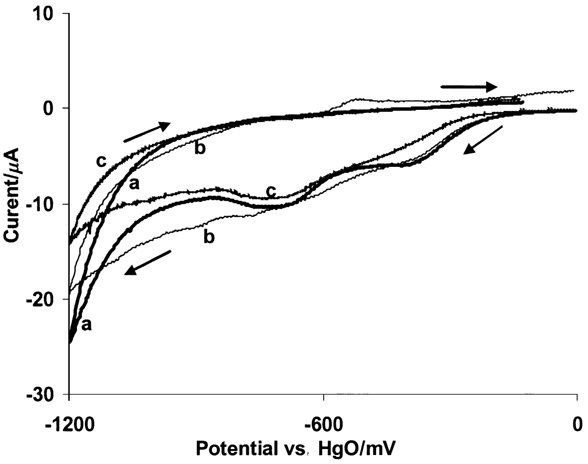

Fig. 8. Typical cyclic voltammograms obtained for the concentrate-CPE (30 wt %) in aqueous solution, $[CN^-]=0.3$ M, pH 10.60. After leaching: (a) Pyrite, (b) Real del Monte and (c) Las Torres. Sweep potential direction initiated from the OCP towards the positive direction and v = 25 mV s^{-1}. Only cathodic zone of voltammograms is shown.

the sweep potential is inverted. The E_λ potential varied from 800 to 1200 mV. For all cases, the inverse potential sweep was inverted again at −1200 mV and the sweep was ended in the OCP value. The importance of this study resides in the demonstration that by increasing the inversion potential during the direct sweep the evolution of the oxidative process is detected. In these cases, the charge associated with the reduction processes is evaluated by quantifying the area under the curve in the cathodic region of the corresponding voltammograms.

A typical E_λ study for pyrite is shown in Figure 9, where several voltammograms at different inversion potentials are presented. The evolution of the oxidation process at inversion potentials above to 900 mV vs HgO may be noted. A very similar behavior is noted in Real del Monte and Acanthite; however, in these cases other peaks, associated with the reduction of silver ions, appear.

In Figure 10, the total charges associated with the reduction of the products formed during the voltammetric oxidation as a function of the maximum oxidation potential (E_λ) are shown for the concentrates (i) and their residues (ii) (pyrite (a), Real del Monte (b) and Las Torres (c)). It may be noted in pyrite (Figure 10(a)) that the values of the total charges of reduction are similar before and after leaching, which indicates that there is practically no modification in the surface leached by cyanidation. According to the AAS results, as well as the metallurgical balance, only 1.5% of the iron was extracted during the leach.

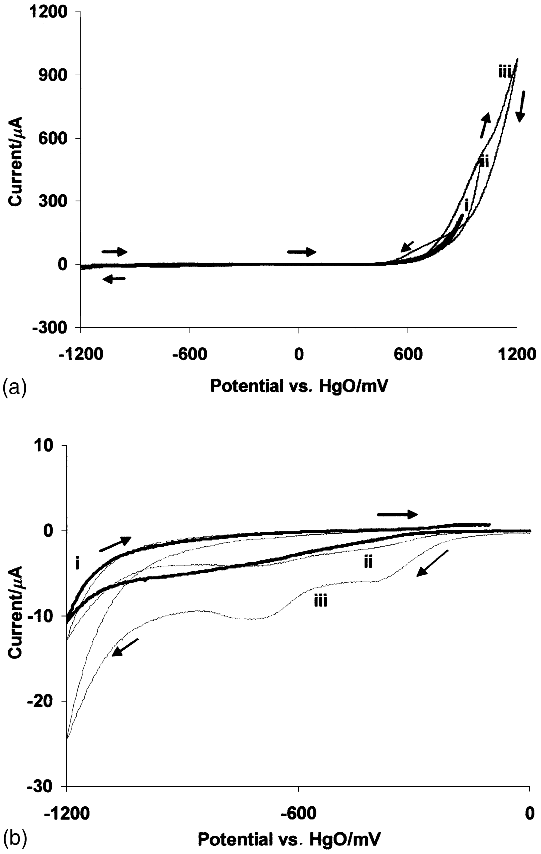

Fig. 9. Typical cyclic voltammograms obtained for the concentrate-CPE (30 wt %) in aqueous solution, $[CN^-] = 0.3$ M, pH 10.60. Sweep potential direction initiated in the positive direction from the OCP (−145 mV vs HgO) until an E_λ value, where sweep direction was inverted. (**i**) $E_\lambda = 900$, (**ii**) $E_\lambda = 1000$ mV and (**iii**) $E_\lambda = 1200$. Cathodic inversion potential was constant at −1200 mV. Sweep rates $v = 25$ mV s^{-1}. (a) Complete voltammogram and (b) cathodic zone.

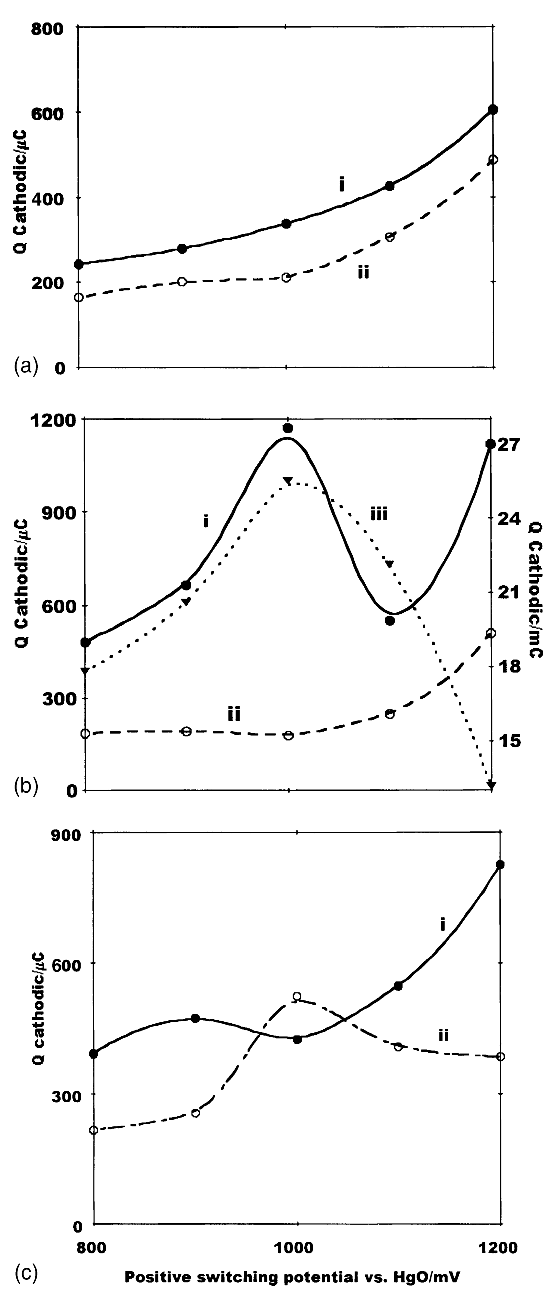

Fig. 10. Total charges associated to the reduction process for the chemical species formed during the voltammetric oxidation for concentrates and their leached residues as a function of the potential where the sweep potential was inverted. (a) Pyrite, (b) Real del Monte and (c) Las Torres. Filled circles (**i**) unleached and hollow circles (**ii**) leaching residues. Acanthite unleached showed in (b) **(iii)** is measured with right-hand vertical axis.

In Real del Monte (Figure 10(b)), there is an large difference between the total reduction charges in the concentrate before and after leaching. It is evident that when the inversion potential is fixed at 800 mV vs HgO, silver sulfide oxidation initiates, which is reflected in the cathodic zone when the silver reduction is detectable. The silver sulfide oxidation becomes greater as the inversion potential is increased, evidenced by a larger total reduction charge of this species. The behaviour shown in the Real del Monte concentrate is confirmed by that found for acanthite (Figure 10(b) **iii**). The manner in which the silver ions produced in the direct sweep are reduced at more positive inversion potentials can be clearly seen. The difference between the values of the total reduction charges in Real del Monte (Figure 10(b) **i**) and acanthite (Figure 10(b) **iii**) may be attributed to the silver contained in each (acanthite 98% and Real del Monte 1.2%). Once the Real del Monte concentrate was leached (Figure 10(b) **ii**), silver sulfide was not detected and for that reason the total charges associated with the reduction processes are similar to those found in pyrite (Figure 10(a) **ii**). This confirmed that the entire original silver content in Real del Monte had been extracted in the cyanidation process, as observed in Section 3.2.

The reduction processes in Las Torres (Figure 10(c) **i**) show few perceptible changes, however, an increasing value of total reduction charges may be observed when the direct sweep potential is increased to values higher than 1000 mV vs HgO. This behaviour can be attributed to a galvanic phenomenon between iron sulfide and the different silver phases, which protects one of the phases from oxidation. Nevertheless, the total reduction charge values are of the same order of magnitude as those obtained in the Real del Monte concentrate (Figure 10(b) **i**) and higher than those for pyrite (Figure 10(a) **i**), confirming the presence of a quantity of silver in the Las Torres concentrate. In the Las Torres residue (Figure 10(c) **ii**), at values of direct sweep potential above 1000 mV vs HgO, the reduction charge shows that there are still some silver species which were not oxidized.

Despite the fact that both concentrates (Real del Monte and Las Torres) contained the same small amount of silver, their presence is detectable; however, their total charges are different. This difference is directly associated with the leachable silver phases. When this method is applied to the residues (Figure 10(b) **ii** and (c) **ii**), it is evident that for Real del Monte there is no silver sulfide remaining since its behaviour is similar to that of the pyrite residue (Figure 10(a) **ii**). In the Las Torres residue (Figure 10(c) **ii**) it can be seen that some silver species are still present in the residue even though the leachable silver phase (aguilarite) was previously extracted. The refractory silver species were identified as freibergite, polybasite and hessite.

4. Conclusions

In the cyanidation of Real del Monte and Las Torres concentrates, which contain the same amount of total silver, different kinetics of silver leaching were observed. Real del Monte showed a faster and more complete silver extraction than for Las Torres, a difference attributed to the presence of different silver phases. SEM analysis of the concentrates before and after leaching established that acanthite is the only silver phase contained in Real del Monte while four different silver phases were detected in Las Torres, aguilarite being the most abundant one. With respect to the leaching residues, the mineralogical characterization showed that aguilarite was the only silver phase leached. The difference in the cyanidation reaction rates between acanthite (Real del Monte) and aguilarite (Las Torres) was probably due to the selenium, in addition to the sulfur, contained in the latter.

Cyclic voltammetry was employed to study concentrate-carbon paste electrodes, permitting qualitative identification of the different oxidative and reductive process for the chemical species present. This method was first applied to two high purity concentrates, the acanthite and pyrite, as limiting cases, and later to the Real del Monte and Las Torres concentrates. Identification of the silver, both leachable and refractory, contained in last two concentrates was possible, even though the total silver represented only 1.2%, proving the sensitivity of this method. Concerning the leached residues, the absence of silver in the Real del Monte residue was evident and its behavior was similar to that obtained for the pyrite concentrate. In Las Torres, a galvanic interference between the silver phases and iron sulfide was observed during the oxidation process, which prevented the identification of the reduction process associated with the aguilarite oxidized in the direct sweep. However, once the concentrate was leached the silver still contained in the residue, such as freibergite, polybasite or hessite, was easily detected. The application of the total charges of reduction associated with the oxidation process allows the quantification of the oxidizable silver species during the direct sweep. This electrochemical method may be proposed to qualitatively detect the silver phases contained in mineral concentrates and to identify those which are refractory in a rapid and reliable manner.

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